

Health & Safety Manual

Supplement 21.14

Safe Handling of Alkali Metals

October 1994

Approved by the ES&H Working Group

_____ date _____
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Safe Handling of Alkali Metals*

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Safe Handling of Alkali Metals

1.0 Introduction

1.1 Purpose and Scope

The chemicals in group 1 of the Periodic Table of Elements are Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), Cesium (Cs), and the unstable decay product Francium (Fr). As a group, these are referred to as alkali metals because they react vigorously with water to form the corresponding hydroxide (e.g., sodium hydroxide), resulting in an alkaline (basic) solution. The alloys of alkali metals are used at LLNL. These alloys are governed by this supplement because they share most of the hazardous properties of the metals.

This group of metals and their alloys demonstrate good electrical and heat conductivity and are often used in their molten state; thus, they are commonly referred to as “liquid metals.” Cesium melts at 28°C—just above room temperature. The NaK alloy most commonly used consists of 78% potassium and is liquid down to -11°C—well below room temperature. All other alkali metals have relatively low melting points and high boiling points (see Table 1 for physical constants).

This supplement covers

- the hazardous properties of alkali metals and their oxides and peroxides;
- engineering and administrative controls and the personal protective equipment necessary for working safely with alkali metals;
- responsibilities of the LLNL organizations involved in the procurement, use, and disposal of alkali metals.

Appendix A contains guidelines for handling waste alkali metals and equipment contaminated with such materials.

1.2 Requirements/Regulatory Summary

Few regulations or consensus standards governing the handling of alkali metals exist. The Federal Occupational Safety and Health Administration (OSHA) regulations make no specific mention of alkali metal compounds as a class or of pyrophoric metals in general, although exposure standards exist for many compounds of these metals. The National Fire Protection Association has no regulations specific to alkali metals or pyrophoric metals, nor do relevant industry (e.g., ANSI, ASTM) consensus standards exist.

Table 1. Approximate physical constants of alkali metals.

	Cs	Rb	K	Na	Li	NaK
Atomic weight	133	85.5	39	23	6.9	17.2*
Melting Point, C	28	39	63	153	179	-11
Boiling Point, C	682	688	760	881	1338	825
Specific Gravity	1.87	1.53	0.86	0.97	0.53	0.73

* The *molecular* weight of other NaK alloys varies depending on the relative concentration of Na and K.

The following standards and regulations govern the handling of alkali metals:

- Standards for alkali metal compounds published by the American Conference of Governmental Industrial Hygienists (ACGIH). These standards are mandated by Department of Energy (DOE) order.
- Code of Federal Regulations, Title 49, Part 173, Section 212, "Hazardous Metal Transportation." This regulation is applicable at LLNL.
- California OSHA Regulation, Title 8, Section 5176, "Pyrophoric Materials." A few common sense requirements from this document are incorporated into this supplement.
- State of California Regulation, Title 22, "Hazardous Waste."

1.3 Applicability

The requirements in this supplement are applicable to any person or organization that purchases, uses, stores, or disposes of alkali metals or their alloys in any quantity.

2.0 Hazardous Properties of Alkali Metals

Pure alkali metals are soft and ductile at room temperature (Cs may be liquid in a warm room) and silver in color (except for Cs, which is golden). These metals are highly reactive and therefore will never be found in nature in their pure state. Pure alkali metals are not considered "toxic" in the usual sense of the word, because it is virtually impossible to inhale or ingest the pure metal. However, reaction products which can be produced when alkali metals come in contact with the human body or other materials can be toxic, flammable, and corrosive. Following are discussions of a few of these reaction products.

2.1 Reaction with Oxygen

Cesium, Rb, and presumably Fr react vigorously with oxygen at room temperature to form the metal oxide, which results in a self-sustaining metal fire that rapidly heats up to almost 1980°C. The element K is less reactive at room temperature and generally will not ignite spontaneously. Na and Li will not result in a fire because they are even less reactive, and oxidation occurs slowly. If these less reactive metals are finely divided or exposed to oxygen in their molten state, spontaneous ignition will occur and a self-sustaining metal fire will develop. In each case, the resulting metal oxide immediately condenses to form a dense, white fume that is highly corrosive to the lungs, eyes, and skin—where metal oxide forms metal hydroxide. These fumes can obscure vision if not contained.

Under various circumstances, alkali metals (except Li and rarely Na) are subject to the formation of higher oxides (e.g., peroxides or superoxides) that may be unstable if cut or scraped. These higher oxides can react with the base metal or organic materials in an explosive manner or can start a fire. In some cases, they may be shock sensitive.

2.2 Reaction with Water

All alkali metals react vigorously with water to form the hydroxide, and the rate of reaction increases as the atomic weight increases. Li reacts the slowest and poses the least hazard. The other metals react very quickly, generating great heat and splattering with the possible destruction of experimental apparatus. Hydrogen gas is also released in this reaction, and the heat can ignite the hydrogen resulting in an explosion. The broad range of explosive mixtures of hydrogen makes this reaction a very difficult problem to control.

2.3 Reaction with Other Materials

Molten alkali metals react with other materials as follows:

- Explosively with hydrogen forming hydrides, which are toxic.
- Vigorously with halogenated hydrocarbons and plastics (Teflon and polyvinyl chloride), possibly creating an explosion and generating toxic gaseous byproducts (phosgene, perfluoroisobutylene, and acid gases).
- Vigorously with organic alcohol (the rate slows as the molecular weight increases), unsaturated organic materials, most inorganic acids, and carbon dioxide.
- Violently with organic acids and mercury.

Lithium reacts with atmospheric nitrogen, nitrogen containing organic materials, and glass at higher temperatures resulting in the failure of glass containers.

3.0 Process for Risk Reduction

Many reactions are possible with alkali metals. Thus, an experimenter planning to use any quantity of alkali metal must perform a careful hazards review of the design, construction, operation, and ultimate decommission of the experiment. Upon completing this review, the experimenter shall contact the area environmental, safety, and health (ES&H) team leader who shall arrange to have the operation reviewed by appropriate discipline personnel (usually an industrial hygienist, a fire protection specialist, and an environmental analyst). Appropriate controls and procedures can be developed from this review, including the need for certain types of ES&H documentation.

The three methods for mitigating the hazards posed by alkali metals are engineering controls, administrative controls, and personal protective equipment. Each of these is further discussed below. In practice, all of these methods are usually implemented when alkali metals are in use. The method required for any experiment is determined by the ES&H evaluation(s) and incorporated into the hazard analysis or operational safety procedure (OSP) (if applicable).

3.1 Engineering Controls

Engineering controls are the preferred means of mitigating the hazards posed by alkali metals. These metals are benign as long as they are kept away from other materials with which they react (e.g., oxygen, water, acids, halogenated hydrocarbons, and carbon dioxide). The fundamental principle is to isolate alkali metals (both in the solid and molten state) from reactive materials.

Lithium, Na, and NaK, and to a lesser degree K, can be transferred in air because the rate of oxidation is fairly slow. All other alkali metals must be transferred in an inert atmosphere, such as in a dry argon-filled or vacuum glove box made of materials that are compatible with the metal, or by other means that prevent exposure to air, water, or other incompatible material. Nitrogen may be used except when handling Li. Similar methods must be used for lighter metals if no amount of oxidation can be tolerated. For guidance on other methods available for the safe transfer of solid and liquid metals, contact Mechanical Engineering or your area ES&H team.

Storage of alkali metals must exclude moisture, oxygen, and in the case of Li, nitrogen. These metals can be stored under mineral oil or in a container that is evacuated or filled with a noble gas. Even under such storage conditions, some oxide or hydroxide may be formed because of liquid or oxygen in the mineral oil or because of leakage into the inert container.

The following engineering controls should be considered, as appropriate:

- Equipment that contains alkali metal must be compatible at the highest anticipated working temperature.

- Packless valves and seamless welded tubing shall be used for liquid systems. Unwelded joints should be encased in a secondary containment (steel-drip trays with oxygen-limiting orifices in a cover).
- Complete secondary containment (steel-drip trays with oxygen-limiting orifices) shall be placed under experimental apparatus that use liquid metals.
- Systems with liquid metals should be designed so that in the event of a shut down, all of the metal flows by gravity to a single low point where it can be removed. A system for removing oxides that may form during the use of liquid metals should be included in the design.
- Where liquid metals other than NaK are in use, adequate heating should be distributed to all parts of the system to prevent the metal from freezing at a cold spot. Electrical trace heating or other means may be acceptable, but steam or water heating is prohibited.
- An adequate ventilation system that is capable of capturing all evolved metal oxide or hydrogen in the worst-case accident scenario shall be provided for operations involving alkali metals. This system shall not exhaust any other hood or piece of equipment, but shall exhaust through a stack that is of such height and location to prevent (1) fumes from re-entraining into building air intakes, and (2) the levels of metal oxide on the roof of the building (or in other areas surrounding the building) from exceeding the threshold limit values established by the ACGIH. A scrubber capable of removing most of the noxious metal oxide in the worst design-base accident may reduce the required stack height. Scrubbers shall be provided with emergency power.
- Systems with liquid metals shall have overpressure vents that are vented into the exhaust system.
- Where quantities of liquid metal exceeding 1 kg are in use, the ventilation system shall have emergency power.
- Inert gas blankets shall have less than
 - 35 mg/m³ of water vapor,
 - 0.5% oxygen,
 - 1.5% hydrogen.

Nitrogen should not be used for operations involving the use of liquid Li.

- Areas where any alkali metal is handled shall be free of sources of ignition. Glove boxes, hoods, or other similar apparatus shall have explosion-proof Class 1, Division 1, electrical systems (if applicable).
- Appropriate leak-detection equipment with alarms should be considered.

- An emergency eyewash/safety shower unit that meets ANSI Standard 358.1-1990 shall be available in all work areas where alkali metals are in use. This unit must be positioned far enough away from alkali metal work so that a system failure will not pose a hazard, but near enough for quick access in the event of an emergency.
- Metal-handling systems shall include features that allow for simplified dismantling and decontamination (see Appendix A for definition).

3.2 Administrative Controls

Extensive administrative controls are necessary in areas where alkali metals are handled. If applicable to your alkali metal operation, the controls below should be stipulated in the OSP where necessary or as appropriate.

Safety procedures. An OSP or a facility safety procedure (FSP) is required for all operations that involve the use of alkali metals in their molten state; all uses of Cs, NaK, and Rb; and any use of Li, Na, or K exceeding 500 g during the entire experiment or for a period of one year, whichever is less. Even if these criteria are not met, the ES&H evaluation may determine the need for an OSP.

Training. All persons handling alkali metals in quantities that require a safety procedure shall complete course HS4260, "Alkali Metal." This course is offered by the Hazards Control Department.

Isolation. General traffic is prohibited in areas where alkali metal operations are performed. The appropriate warning signs shall be posted in these areas limiting access to authorized personnel. Further access controls, up to and including run-safe boxes, may be necessary and should be stipulated in the OSP.

Storage. Only the amount of alkali metal necessary to perform the work shall be removed from storage. Spare materials shall be returned to the appropriate storage container, and the container to its appropriate location. Metals shall be stored in the containers supplied by the manufacturer (or as stipulated in the hazard review or OSP) under mineral oil or in an inert atmosphere or a vacuum. Storage containers must indicate their contents, the hazards properties, date received, weight of the metal, and type of oil or gas used to inert the metal. The storage area must be free of combustibles that would ignite in the event the metal did burn and of sources of ignition. No source of water (sprinklers, showers, sinks) shall be in the immediate proximity of the metal. The storage area must also be prominently marked to indicate the presence of alkali metals. Up to 5 kg of alkali may be stored in a flammable storage locker inside a building. Quantities exceeding 5 kg must be stored in separate structures that are noncombustible (e.g., steel transportainers).

Handling Alkali Metals. Skin and eye contact with alkali metals must be avoided. Where possible, tongs or other appropriate tools must be used to handle solid alkali metals; syringes or other means should be used for liquid metals to prevent skin contact (see discussion in this section). Oxidized materials (white surface coating) may make the metal more hazardous to handle. Materials with a yellow or orange coating may indicate the presence of peroxides or superoxides, which may be explosive if cut or abraded. These materials should not be used; they should be isolated and disposed of promptly. Contact your area ES&H team for further guidance.

All tools used to handle alkali metals must be dry, rust-free, clean, and composed of a material compatible with the metal. Tools can be dried by baking in an oven, desiccating in a vacuum, or rubbing with anhydrous dry soda ash.

Containers with alkali metals shall be assumed to contain flammable hydrogen gas in the headspace, even if stored under mineral oil or inert gas. Thus, no source of ignition shall be present where these containers are opened. Tools used to open the containers shall be of the sparkless variety.

Fire and Spill Emergency Preparedness. The appropriate material shall be available to extinguish fires and contain alkali metal spills. Anhydrous dry soda ash may be used for all metals except Li. This material must be kept in a sealed yellow container that is properly labeled. Lith-X fire extinguishers must be used for Li. Alternative extinguishing agents such as powdered graphite or the commercial Met-L-X metal fire extinguishers may be used. Employees involved in metal work must be trained in the use of these extinguishing materials.

Only trained personnel using personal protective equipment (as specified in the OSP or other hazard review document) shall attempt to control small, contained fires or spills. If fumes are escaping into the breathing zone of these personnel, no local employee shall attempt to extinguish the fire. Large or uncontained fires or spills, or fires where the ventilation system does not contain all of the fumes, shall be handled only by the Fire Department. Before attempting to extinguish a metal fire or contain a spill, notify the fire dispatcher (dial 911).

Skin or Eye Contact Emergency Preparedness. If any alkali metal fragment or drop enters the eye, it will immediately generate considerable heat which will likely result in severe eye damage. In such cases, the eyes shall be flushed with water from an eyewash/safety shower that meets the requirements of ANSI Standard 358.1-1990. Continue to flush the eye with water while someone dials 911 for emergency help.

When alkali metal comes in contact with the skin, the first response is to strip off all contaminated clothing. Other responses depend on a number of factors. If contact with the metal occurs at only one or two spots on the skin, it is best to wash off those areas with mineral oil. A container with at least one quart of mineral oil, or as specified in the OSP, shall be available in alkali metal work areas. If contact with the metal is widely distributed over the body, a decision on the best course of first aid must be made immediately. If the material is already burning (molten alkali metals with all-burn solid Rb and Cs will burn spontaneously), the victim should be drenched continually under a

safety shower that meets the requirements in ANSI Standard 358.1-1990 until emergency help arrives. If the material is not burning (perhaps Na or Li scraps), the metal should be removed by wiping the skin with mineral oil. In all cases, dial 911 for assistance.

Procurement. Experimenters shall purchase all alkali metals through the Services and Distribution Department, noting the pyrophoric nature of the material on the requisition (Form LL-2350-2). The Materials Management Section of the Mechanical Engineering Department shall receive and deliver all alkali metals in their original containers to the requester. Li, Na, and K in quantities greater than 500 g, including any quantity of Rb, Cs, and NaK (or other alloy), shall only be released upon receipt of a valid OSP governing the use of those materials. These materials will not be released if the OSP is not available.

Transportation. In addition to meeting all shipping requirements, alkali metals shall always be transported in their original containers. The Materials Management Section shall transfer alkali metals (except for hazardous waste) between buildings or onsite or offsite. Specific details on packaging these materials for transportation are available from the Materials Management Section.

3.3 Personal Protective Equipment

Engineering controls greatly reduce the need for personal protective equipment when handling alkali metals. Under all circumstances where alkali metals are in use, the following are required as a minimum:

- An easily removable laboratory coat (or equivalent)
- Chrome leather gloves or appropriate rubber gloves
- Faceshield

Where solid metal is handled without a barrier (e.g., glove box), a fire retardant apron and goggles are required. Additional personal protective equipment shall be stipulated in the OSP in cases where large quantities of solid alkali metals or liquid metals are in use.

4.0 Responsibilities

4.1 Room Responsible Person/Lead Experimenter

The room responsible person/lead experimenter shall

- ensure that
 - a complete ES&H evaluation of the proposed operation is conducted in accordance with Chapter 2 of the *Health & Safety Manual* before starting the experiment. The initial review shall be conducted by the experimenter, with subsequent review by members of the ES&H team.

- where required, personnel who work with alkali metals complete course HS4260, “Alkali Metal Safety.” This course is offered by the Hazards Control Department.
 - where required, an engineering safety note (ESN) is developed and referenced in the OSP in cases where liquid or solid metals are used and the safety analysis indicates the need for an ESN.
 - all requirements of the ESN and OSP are complied with.
 - employees follow the procedures specified in this supplement for all purchases of alkali metals. Purchases shall be made through the Services and Distribution Department, and the requisition should indicate that an alkali metal is being purchased.
 - the storage, handling, and disposal of alkali metals meet the requirements of this supplement and other LLNL regulations.
 - all engineering controls (e.g., ventilation, inerting gases) function properly.
 - only appropriate types of fire extinguishers are present in the immediate alkali metal work area.
 - first-aid equipment is available in alkali metal work areas.
- prepare an OSP for all uses of molten alkali metals; for solid Li, Na, or K that exceeds 500 g during the entire experiment or for a period of one year, whichever is less; for any amount of Cs, Rb, or NaK; or where the ES&H evaluation so indicates;
 - prepare a conduct of operations report and safety analysis documentation if the hazards analysis so indicates;
 - contact the area ES&H team before cleaning or dismantling any liquid metal handling system, unless procedures for such are already addressed in an OSP.

4.2 Hazards Control Department

The Hazards Control Department shall

- conduct hazard reviews of proposed, new uses of alkali metals when requested or as required;
- assist in the design of safety-related systems and in the preparation and review of OSPs;
- review ESNs associated with liquid metal systems;
- administer course HS4260, “Alkali Metal Safety,” as required;
- evaluate roof access classification changes that may result from the use of alkali metals;

- review the implementation of hazard mitigation procedures and of the equipment, and notify the room responsible person/lead experimenter of any deficiencies;
- respond to spills, fires, exposures, or other emergencies involving alkali metals;
- review all requisitions for alkali metals received from the Services and Distribution Department in accordance with the requirements of this supplement;
- ensure that the Fire Department is equipped to handle large-scale alkali metal fires onsite at all times.

4.3 Materials Management Section

The Material Management Section of the Mechanical Engineering Department shall

- receive alkali metals in accordance with the guidance in this supplement;
- inspect incoming shipments of alkali metal containers for signs of failure (e.g., leakage). Notify the area ES&H team if a container is damaged or corroded, or call 911 if a spill occurs;
- provide an appropriate storage area for alkali metals (see Section 3.2);
- deliver the alkali metal to the requester in its original container only after receipt of a valid OSP describing the use of the metal as needed;
- comply with DOT transportation requirements for alkali metals.

4.4 Environmental Protection Department

The Environmental Protection Department shall

- conduct a hazard review to evaluate environmental contamination problems, permit requirements, NEPA declarations, and other environmental issues during the experimental design phase;
- specify requirements for packaging waste alkali metals or equipment contaminated with such materials;
- remove and dispose of packaged waste alkali metals;
- properly handle contaminated equipment for disposal.

4.5 Facility Manager

The Facility Manager shall

- maintain awareness of all operations involving alkali metals in his/her area of cognizance;
- contact his/her ES&H team to determine if the roof access classification of the building has changed. This is required for areas whose alkali metal system has a ventilation system.

4.6 Health Services Department

The Health Services Department shall

- specify first-aid requirements for accidental exposures that involve alkali metals or their oxides or hydroxides;
- maintain appropriate facilities for immediate support of individuals exposed to alkali metals or their alloys.

4.7 Mechanical Engineering

Mechanical Engineering shall assist experimenters in the preparation of ESNs pertaining to the design of alkali metal handling systems.

5.0 LLNL Contacts

Contact the following, as appropriate, for further guidance or additional information:

- ES&H team (the telephone number for each team varies by area)
- Industrial Hygiene Technical Leader, ext. 2-1214
- Chemical Hygiene Officer, ext. 2-1214
- Materials Management Section, ext. 2-5634
- Hazardous Waste Management Division, ext. 2-1996

6.0 Supporting References and Standards

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Appendix A

Guidelines for Handling Equipment Contaminated with Waste Alkali Metals

A.1 Disposal of Waste Alkali Metals

Waste alkali metals or equipment contaminated with such materials must be packaged in accordance with DOT requirements. Contact your area ES&H team or the hazardous waste technician for specific guidance.

A.2 Decontaminating, Recycling, and Disposing Contaminated Equipment

Equipment contaminated with alkali metals must be decontaminated before recycling. Decontamination is usually only a problem when the metals are used in the molten state. Some equipment may contain oxide, peroxide, or superoxide residue, which pose additional hazards during the decontamination and disassembly process. This process may need to be addressed in an OSP. General procedures are described below.

- Drain all alkali metal from the system.
- Make sure the system has no cold spots that may cause residual metal to freeze or prevent low points from draining.
- Compare the weight of the metal in the system to that removed, and account for any large loss before proceeding.
- Purge the system with inert gas (do not use nitrogen for Li) and carefully dismantle the system. Look for residual metal or white, yellow, or orange discoloration that may be indicative of dangerous oxide or superoxide deposits. The use of steam or alcohol to purge the system is potentially very hazardous. In cases where purging is desired, an OSP must be prepared.
- Do not dispose used materials as hazardous waste. Such materials shall be sold for scrap or recycled where possible.